

ADIABATIC DEWAR CALORIMETRY:
SYNTHESIS OF
AUTOMATE YELLOW 96

TO : U.S. Chemical Safety & Hazard Investigation Board
2175 K Street N.W.
4th Floor
Washington, DC 20037

F.A.O.: Mr. David Heller

Prepared By

Scott M. Ferguson
Sr. Laboratory Technician

Reviewed By

Charles Gilbert
Sr. Chemist

Approved By

Richard C. Wedlich
Sr. Process Safety Specialist

FOR AND ON BEHALF OF CHILWORTH TECHNOLOGY, INC.

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1. Objective

To quantify the magnitude of any exothermic activity and gas generation in a chemical system under the conditions normally encountered during large-scale manufacturing should cooling or stirring fail during a critical stage of processing.

2. Method

Prior to testing the pressure transducer was calibrated to ensure accuracy of the measurements. The reactants (1-chloro-2-nitrobenzene and 2-ethylhexylamine) were charged to the Dewar calorimeter, which was then positioned inside the oven in the blast room. The pressure transducer, thermocouples, heating element and stirring drive were connected to the Dewar and the oven and blast room doors were closed.

The sample was heated via an internal coil, at approximately 1° C/min until it produced an exothermic response. Upon entering into an exotherm the internal heater was shut off and the sample allowed to exotherm while the oven followed the exotherm.

3. Test Apparatus

The test was performed in a low heat loss Dewar vessel that is of stainless steel construction. The bursting pressure of the Dewar is >500 psi (>34 bar). The vessel was closed to the atmosphere. The calorimeter was placed in an adiabatic shield oven in which the temperature of the vessel surroundings was controlled to ensure that there was no heat flow through the walls of the calorimeter. The oven was located in a 'blast room' capable of withstanding rupture of the vessel and release of the chemicals. The Dewar was controlled remotely throughout the experiment.

The calorimeter is shown in **Figure 1** and a schematic of the installation is shown in **Figure 2**.

4. Sample Information

Company name	:	U.S. Chemical Safety & Hazards Investigation Board
Source of Samples	:	Purchased from Aldrich®
Test Date	:	4/11/00
Operator	:	S. Ferguson
Sample Conditions	:	Samples were run 'as-received'

Table I: Reactant data

Reactants	Charge Amounts	
	Moles	Grams
1-Chloro-2-nitrobenzene	1.42	233.7
2-Ethylhexylamine	2.84	367.07

5. Results

Tables II & III: Exotherm data

T₀ (°C)	P₀ (barg)	M₀ (°C/min)	T_F (°C)	DT (°C)	P_{ULT} (barg)
90	0.36	1.47	400	310	8.86

T⁰_{MAX} (°C/min)	T @ T⁰_{MAX} (°C)	P⁰_{MAX} (barg/min)	TMR (min)
7874*	267.04	98.5*	34.6

*Due to the violent nature of the decomposition the reaction may have reached rates above that which was measured.

Table Legend

T₀	–	Exotherm Onset Temperature
P₀	–	Exotherm Onset Pressure
M₀	–	Exotherm Onset Rate
T_F	–	Final Exotherm Temperature
DT	–	Exotherm Temperature Rise
P_{ULT}	–	Ultimate Exotherm Pressure
T⁰_{MAX}	–	Maximum Self-heat Rate
T @ T⁰_{MAX}	–	Temperature at Maximum Self-heat Rate
P⁰_{MAX}	–	Maximum Pressure Generation Rate
TMR	–	Time-to-Maximum Rate

6. Interpretations

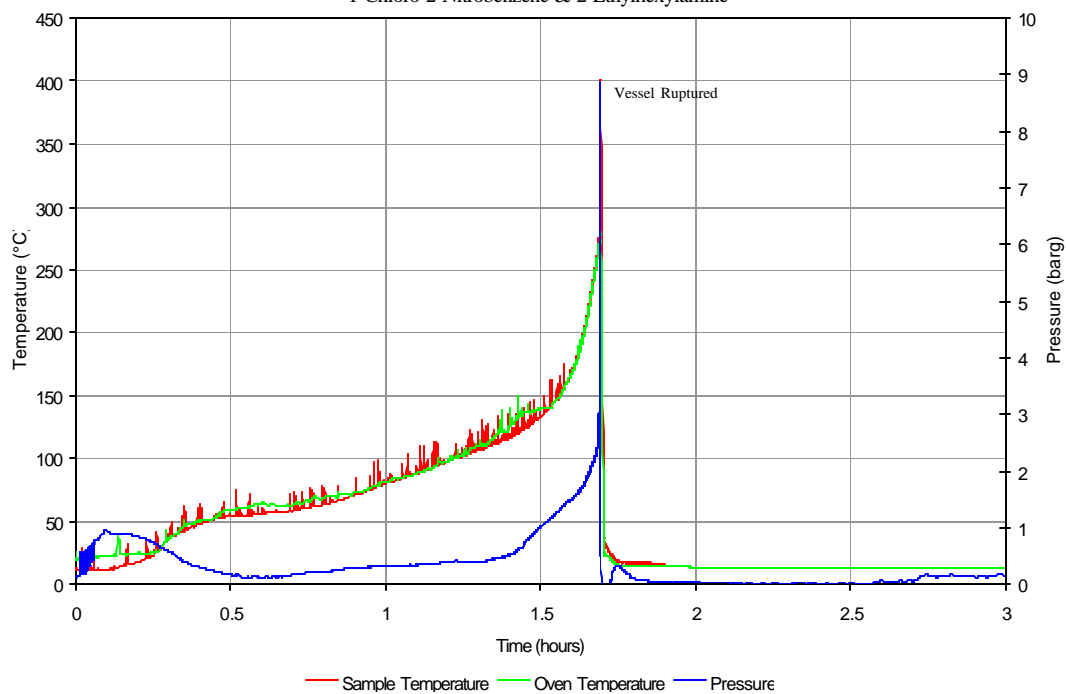
Time-Temperature-Pressure data from the run is shown in **Graph 1**. The Antoine plot is shown in **Graph 2**.

Adiabatic Dewar testing of the reaction of 1-chloro-2-nitrobenzene and 2-ethylhexylamine to form Yellow 96 is complete. As was previously thought, results indicate that under near adiabatic conditions the reaction poses a significant hazard. Approximately 1 hour and 42 minutes into the test and 35 minutes into the exotherm the reaction exploded violently, fragmenting the Dewar, destroying oven and stirring motor, releasing chemicals and shrapnel into the blast room and shearing off the sprinkler head located in the ceiling of the room.

The reaction began self-heating 67 minutes into the test at approximately 90° C. The exotherm continued to a maximum temperature of 400° C and a maximum recorded pressure of 130 psig (8.84 barg). However, the maximum pressure reached during the test was far greater than this. The reaction generated pressure at a rate greater than the computer could track. It should also be noted that the maximum temperature that could be recorded by the software was 400° C. The reaction may have reached temperatures above this.

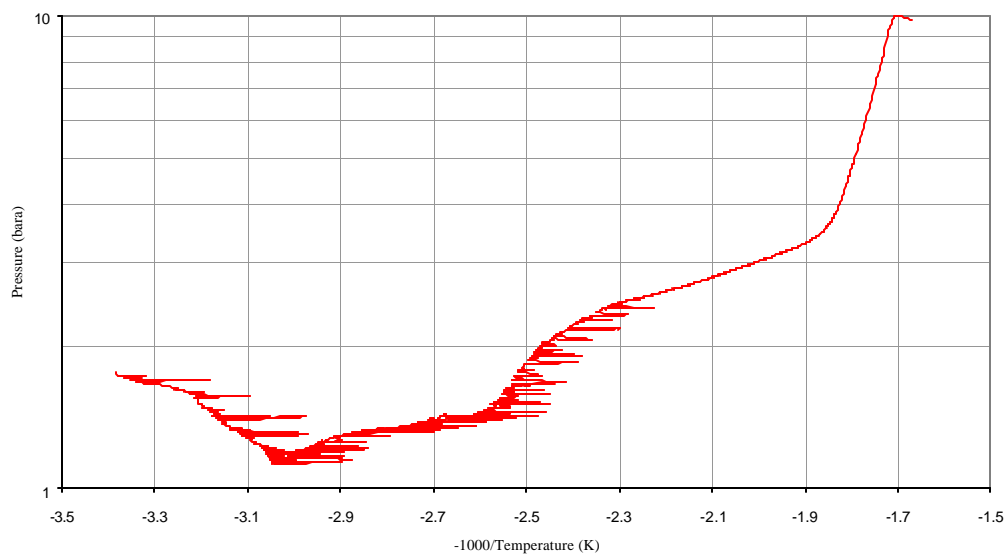
Graph 1

Adiabatic Dewar Testing:
U.S. Chemical Safety & Hazards Investigation Board
1-Chloro-2-Nitrobenzene & 2-Ethylhexylamine



Graph 2

Adiabatic Dewar Testing:
U.S. Chemical Safety & Hazards Investigation Board
1-Chloro-2-Nitrobenzene & 2-Ethylhexylamine



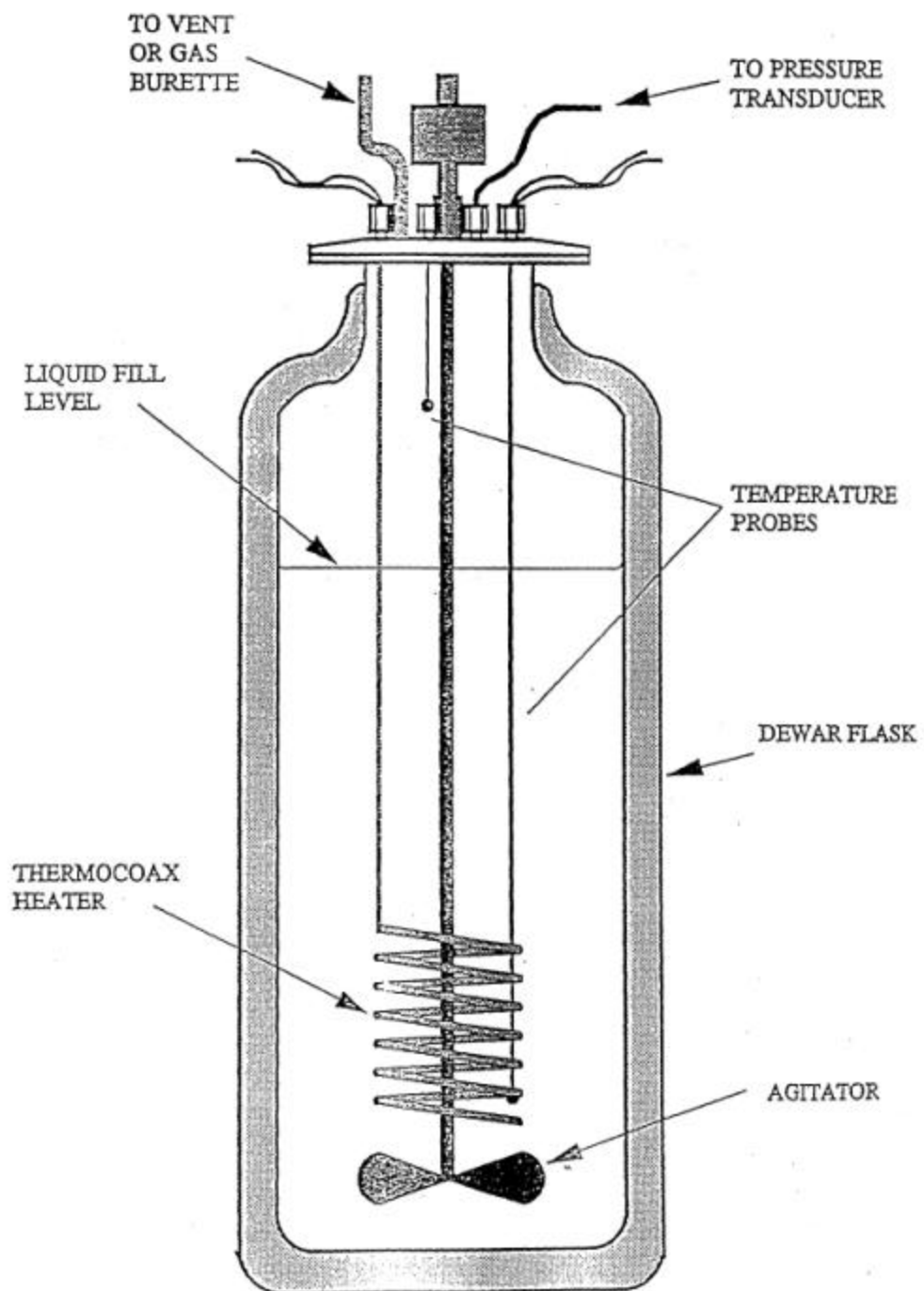


Fig 1 : Adiabatic Pressure Dewar

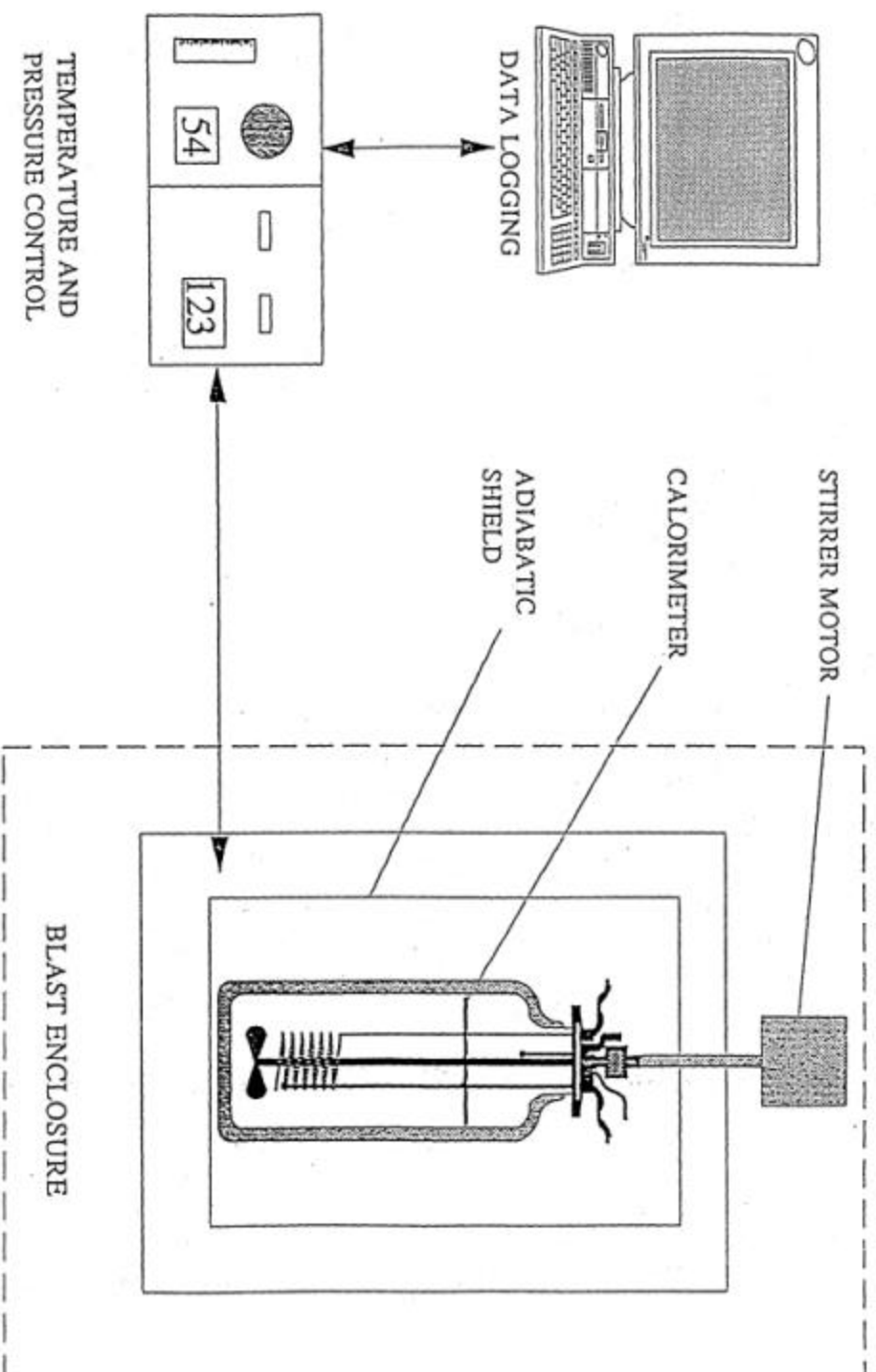


Fig 2 :- Dewar Calorimeter Installation